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Anomalous Diamagnetism and Crystal Structure

By

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1. *Introduction.*

In two famous memoirs on "Thermomagnetische Eigenschaften der Elemente", Kotaro Honda and Owen[1] had observed the remarkable phenomenon that graphite shows a rapid diminution of susceptibility with temperature. Thus graphite with a value of about $-4{\cdot}9^*$ sp. χ at atmospheric temperature falls down to about $-1{\cdot}2$ at 1000° C. Bismuth and antimony having an anomalous diamagnetism of about $-1{\cdot}3$ and $-0{\cdot}8$ at atmospheric temperatures, show a decrease on heating and a sudden diminution on melting.

Bismuth and antimony are also anomalous in that their diamagnetism in combined state is many times smaller than in the solid state. Graphite in particular and also the two other elements exhibit a high degree of anisotropy. It is also a curious fact that the other allotropic modifications of carbon have a very small susceptibility compared with that of graphite. Is anomalous diamagnetism then not an atomic property ?

[1] Kotaro Honda and Owen, Ann. der. Phys. **32**, 1027, 1910 and **37**, 657, 1912.

* In the paper, the susceptibilities are throughout expressed in the unit of 10^{-6} and should be multiplied by the factor.

Closely connected with the diamagnetic property of graphite and amorphous carbon is the X-ray phenomenon observed by Debye and Scherrer, that whatever may be the form of amorphous carbon, the diffraction maxima occur at about the same angle as in the case of graphite but much more diffuse. We have also the experiments of Asahara[2] on graphite and colloidal graphite. He has observed that when graphite was colloidalized for a number of days and the fine particles were investigated, there was no powder pattern, but only a broad diffuse ring as liquids give near their critical temperature. If anomalous diamagnetism is due to crystal structure, then a decrease should be observed on colloidalization according to X-ray evidence.

We have already the hypothesis of Ehrenfest[3] that the high diamagnetism of bismuth is due to the large electron orbits in the crystal lattice and that of Raman,[4] that the same hypothesis might explain the diamagnetism of graphite.

It was thus thought important to examine the diamagnetism of the colloids of anomalous diamagnetics. There is no literature on the subject, but there is a single observation of Honda and Owen in the memoir referred to, where the diamagnetic susceptibility of "regulus" bismuth is given as 1·34 and that of colloidal bismuth 0·495. This curious fact has not been noted at all; probably the discrepancy was thought to be due to impurities as in many magnetic observations.

It is hoped that a thorough investigation of the diamagnetism of the colloids, the anisotropy, the electrical and the thermal conductivities in the different directions of the crystals may serve to elucidate the problem of anomalous diamagnetism completely. The present paper only deals with the first property of the three anomalous diamagnetics: graphite, bismuth, and antimony.

[2] Asahara, Sc. Papers of the Institute of Physics and Chemistry Research, Tokyo. 1, 23, 1922-23.

[3] Ehrenfest, Physica 5, 388, 1925.

[4] Raman, Nature, 123, 945, 1929.

2. *Experimental.*

The magnetic balance was of the Curie type, the torsion in a quartz fiber produced by the diamagnetic force being read by the deflection of the mirror as in the ordinary lamp and scale method. The deflections were kept small and in most cases the weight of water or standard substances was so adjusted, that the deflections were nearly equal and the retorsion method was not employed.

A large electro-magnet with inclined pole pieces gave the field. Precautions were taken to keep the current constant and obtain accurate values, the arrangements being similar to that the author employed during the investigation of vapours.[5]

When the diamagnetic property of highly anisotropic substances is determined, it is necessary to avoid the collision of the capsule with the walls of the balance chamber, as otherwise it leads to serious errors due to orientation of the crystals.

Special precautions were taken to avoid convection current and to secure accuracy. The susceptibilities are those obtained at atmospheric temperature, nearly 30° C.

(*a*) *Investigations on Single Crystals of Graphite.*

Crystal 1, weight 0·075 gram.

Crystal direction.	Deflection.	Sp. χ	
C $\perp$ F and horizontal	18	2·86	High field
C $\perp$ F and vertical	17·5	2·78	
C $\parallel$ F	92·5	14·9	

Magnetic anisotropy 5·27, mean sp. χ $\frac{a+b+c}{3}$; 6·85

[5] Vaidyanathan, Ind. Jour. Phys., **2**, 135, 1927.

Crystal 2, weight 0·16 gram.

Crystal direction.	Deflection.	Sp. χ.
C ⊥ F	7·3	2·7 Low field.
C ∥ F	49	18·09

Magnetic anisotropy = 6·7, mean sp. χ = 7·83.

Crystal 3, weight 0·0501 gram.

Crystal Direction.	Sp. χ.	
C ⊥ F	3·11	Low field.
C ∥ F	17·0	

Magnetic anisotropy = 5·5 mean sp. χ = 7·94.

(b) *Determination of the Absolute Value of Graphite Powder (purified).**

Weight.	Deflection.	Sp. χ.
·04 (graphite)	25 divisions.	
·083 (graphite)	47·5 ,,	
·310 (water)	23·5 ,,	
Empty capsule	2·5 ,,	
·550 (water)	46 ,,	5·12

Ceylon graphite was well powdered and purified in hydrochloric acid to remove iron. The purification was carried out a number of times until the filtrate gave no test with potassium thiocyanate. The graphite after purification was dried thoroughly and used in subsequent investigations. The absolute value of pure graphite was determined in comparison with that of water.

* Due to the fact that the author was appointed as reader in the Annamalai University, though the work was started at Calcutta, it was carried out in the University Laboratories. The electric source in the latter being only a battery of 110 Volt, the observations on different days were not constant due to the fluctuations of the battery charge. It therefore became necessary to repeat the standard substance, the 'regulus' and the colloid at every observation to avoid uncertainties. This has been done using a sensitive ammeter.

With a view to thoroughly examine the various effects on graphite, the following investigations were made.

(*c*) *Influence of mechanical disturbances.*

The capsule was so arranged that it was not free to orient about its own axis.

1. On pressing, the specific susceptibility was 3·91
2. On tapping in a magnetic field of about 20,000 gauss ... 2·12
3. When the capsule was turned at right angles to that in position 2 ... 7·0
4. After disturbance ... 4·3

(*d*) *Influence of colloidalization.*

The purified sample of graphite was then mechanically colloidalized. The powder was treated with a one per cent. solution of tannic acid and finely powdered in an agate mortar for a number of days. This was then stirred continuously for about a fortnight with a mechanical glass stirrer fitted with paddles. These were then allowed to settle for about a week. The different layers were taken off and centrifuged or sometimes allowed to sediment for weeks. The weights obtained were generally small being about 0·01 to 0·02 gram and the susceptibility of these different specimens was determined.

Weight.	Deflection.	Sp. χ.
0·025	20·5	4·98 powder.
0·029	16·5	3·2 0·8μ
0·013	4·7	2·2 very violent motion in the high power microscope.
0·021 ?	2·5?	2>1 One month sedimentation.
[6] 0·013	+1	? Spongy mass decanted and evaporated.

[6] In this case it may be that the apparent paramagnetism is due to the absorbed oxygen from the atmosphere, since the small weights are obtained by slow long and cumulative processes. Similar observations have repeated during 2 or 3 independent colloidalizations.

To determine the source of error due to tannic acid, its susceptibility was determined.

0·05	3·75	0·75

Since only a one % solution was employed the susceptibility due to the whole weight of the tannic acid was 0·075 and hence too small to affect the value of graphite to any appreciable extent.

(*e*) *Cane sugar charcoal, purified (amorphous).*

Weight.	Deflection.	Sp. χ.
0·15	11·3	0·60
0·209	14·9	0·57
		mean 0·585

In order to test the ash content of sugar carbon 0·3 gram of the substance was heated and gave 0·0005 gram of ash. This is 0·12% ash content and gave no test for iron.

(*f*) Another important point that suggested itself was that if the microcrystals orientated in the field, the decrease of susceptibility might be apparent and purely a directional effect. In order to test this point a small lump of graphite was mixed with canada balsam, and the susceptibilities of the mixture and constituents were measured separately. The canada balsam holds together the small particles and does not allow any orientation. The following results were obtained.

Weight.	Deflection.	
0·063	64	graphite.
0·107	70	mixture with canada balsam.
0·840	49·5	canada balsam.
0·500	78	canada balsam.

In the mixture, 0·044 gram of canada balsam causes

a deflection of 7 mm. as in the pure substance and hence the effect is purely additive and there is no orientative effect of the micro-crystals.

(*g*) *Effect of heat.*

In order to examine qualitatively, the effect of heat on pure powdered graphite, the specimen was heated up to about 400°C the susceptibility showing a decrease. This was in conformity with the observations of Honda and Owen.[7] The object in repeating the same was only to examine if the decrease they observed was due to impurity, since I took special precautions to purify the substance.

(*h*) *Experiments on antimony and its colloids.*[8]

Weight.	Deflection.	Susceptibility.	Physical state.
0·38	46	0·72	Water.
0·19	25	0·779	'Regulus' Kahlbaum
0·24	29	0·707	6μ Antimony.
0·32	28·5	0·535	150μμ } Compared
0·297	34·5	0·72	Water } immediately.
0·0225	0		Ultra-microscopic. „
0·023 (regulus)	4·2	0·779	

(*i*) *Experiments on antimony compounds.*[9]

Compound.	Mol. sus.	Ionic. sus.
$SbFe_3$	45·5	Sb^{iii} 26·3
$(C_6H_5)_3Sb$	182·2	Sb^{iii} 25·9
$(C_6H_5)_3Sb(OH)_2$	238·3	Sb^{v} 66·9

[7] *Loc. cit.*

[8] Antimony and bismuth were colloidalized as graphite, but the process was continued much longer.

[9] Tables Annales, Internationale de constantes, Vol. V, Part I, 797, 1925.

(j) Experiments on bismuth and its colloids.

Weight.	Deflection.	Susceptibility.
0·179 Bismuth "regulus"	8·5 low field	
0·342 Water	11 " "	1·17 (mean) Compared immediately.
0·179 Bismuth "regulus"	41 high field	
0·342 Water	51 " "	
0·081 (·5μ) bismuth	10·5	0·598 "
0·081 "Regulus" bismuth	20·5	1·17 "
0·120 Arced in distilled water [10]	7·5	0·286 "
0·120 "Regulus" bismuth	30	1·17 "

(k) Experiments on bismuth compounds.

Substance.	Sp. χ.	Molecular χ.	Ionic sus.
Bismuth nitrate, $5H_2O$	0·329	159·2	43·4 Bi^{iii}
Bismuth trisulphide	0·284	144·3	45 "
Bismuth selenide	0·284	184·9	54 "
[11] $Bi(C_6H_5)_3$		196·9	40·6 "
[11] $(C_6H_5)_3Bi(NO_3)_2$		254·5	69·8 Bi^{v}

3. *Discussion of Results.*

The two theories, one that of Schrodinger and the other of Langevin, do not explain the anomalous diamagnetism. According to the former theory, the electrons are considered

[10] In the case of arced bismuth it is possible that such a low value might be due to the formation of the oxide and the fine powder consisting of the mixture.

[11] Tullio Gnesseto et Maria Binghinotto, *Atti. R. Inst. Veneto*, **72**, 1515, 1914, and *Tables Internationale de Constants*, *Vol. IV, part 2*, 667, 1922.

as free as the molecules of a gas and the expression for the volume susceptibility is $\chi = -\frac{1}{3}\frac{ne^2\lambda^2}{m}$. Simple calculation shows that this is far too small for elements having small conductivities. Only in elements having a very high conductivity does the contribution come to nearly of the same order as that due to Langevin theory. Of all the metals it is curious that antimony and bismuth have the smallest conductivity and graphite has a conductivity of the same order as bismuth. The following are the conductivity values at atmospheric temperatures:

Graphite[12]	$0{\cdot}002 \times 10^6$	Best specimen. Values vary.
Bismuth	$0{\cdot}0084 \times 10^6$	
Antimony	$0{\cdot}025 \times 10^6$	
Copper[13]	2×10^6	

The theory of free conducting electrons, so successful in explaining conductivity, does not then seem to be applicable in this case. In the case of graphite, Koenigsberger [14] has measured the thermal conductivity also, obtaining a value of 0·85 (Cal/Cm. sec. °C.) which is nearly equal to that of copper and the substance therefore does not obey the law of Wiedemann and Franz.

According to Langevin theory, the diamagnetism is atomic and hence cannot explain the thermal, colloidal and chemical changes of diamagnetism.

But as suggested by Ehrenfest [15] and Raman [16] if we attribute the high diamagnetism to the lattice electron orbits, we may understand these phenomena more clearly.

[12] Roberts, Phil. Mag., 23, 153, 1913. The paper contains a beautiful account and summary of some of the properties of graphite.

[13] The value of copper is given only for comparison.

[14] Koenigsberger and Weiss, Ann. der. Phys. 35, 123, 1910.

[15] *Loc. cit.*

[16] *Loc. cit.*

(1). *The Different Valencies of Graphite and its X-ray Structure.*

The structure of graphite has been ascertained by X-ray analysis, (see Bragg, X-rays and Crystal Structure). The distance between the vertical layers (*i.e.* along the *c* axis, is 3·40A and between the carbon atoms in the horizontal layers is 1·5A. The basal planes or planes of cleavage are hexagons as in the case of the benzene ring and according to Bragg, there is a concrete existence for these rings in graphite. The crystal structure is rhombohedral. But here the four valencies of graphite unlike those of diamond are differentiated into a 3+1 valency. The single or the fourth valency is supposed to be directed upwards between the different layers and this is long and weak. The cleaving and lubricating tendencies of graphite are supposed to be due to this weak mobile bond. Thus a change in the shape of the atom is accompanied by the change in the crystalline form.

As mentioned in the introduction, the amorphous carbon derived from different sources showed itself to be microcrystalline graphite.[17] The larger diffuseness in the X-ray patterns of the amorphous variety as compared with that of graphite is explained by Debye and Scherrer as analogous to the case of a grating with a few lines in it, resulting in a smaller resolving power. But all forms of amorphous carbon have a susceptibility much smaller than that of graphite and so the susceptibility of graphite must depend also on the number of aggregate atoms in the microcrystal and this is what the present investigation on colloids indicates.

(2). *The 3+1 valency of graphite and its diamagnetism.*

According to the orbital theory of diamagnetism $\chi_A = -\frac{Nne^2}{6mc^2}\overline{r_1^2}$, the letters having their usual significance.

[17] Debye and Scherrer, loc. cit. (Bragg, X-rays and Crystal Structure).

If the fourth valency in graphite is directed between the different vertical layers, the diamagnetism in this direction (C⊥ F) must be the contribution from this orbit since the other 3 valencies are in the horizontal plane. The atomic susceptibility in this direction as determined by the average of the single crystal determinations is 35 and by simple calculation the radius comes out as 3·49A. Thus the magnetism-diameter 6·98A is twice the distance between the layers (3·40A) given by X-rays.

These facts can only be reconciled if this mobile bond goes to the alternate layer in its orbital circuit in the crystal. It is natural to suppose that this circuit is even longer, for we get the radius of the orbit from the assumption that it is circular according to the theory. If it is elliptic with the major axis ‖ the *c* axis, it may comprise the atoms in 4 or 5 vertical layers, but it cannot be uniquely determined from magnetism. These single valencies must also be paired with those of atoms in the different layers, as otherwise a single valency orbit ought to exhibit paramagnetism in this direction, the diamagnetic contribution of the K shell being very negligible.

In the *ab* plane, the atomic diamagnetism reaches a very high value being 210 per gram atom. According to the orbital theory of diamagnetism, the contribution here is due to the three-valency electrons in this plane. Applying the orbital theory, the radius of the orbit comes out as 4·8A. The X-ray radius of each atom in this plane is 0·75A and therefore the total number of atoms enclosed by the orbit in the hexagonal plane is $\frac{4\cdot8^2}{0\cdot75^2}$ or 45 atoms. (The magnetic radius of atomic carbon in combination or from diamond is 0·59A). As graphite is typical of aromatics, such an orbit must comprise about 16 benzene rings. These orbits form a net-work of large equipotential surfaces in the crystal lattice in the plane of the hexagonal ring as truncated prisms. It is only necessary in this case to conceive of the valency electrons

of the different atoms to touch each other and go round in unobstructed paths in the crystal lattice. These might also link the different molecular groups and thus form the conducting surfaces. Such a theory would indicate that in graphite when the macrocrystal groups are subdivided by heating [18] or colloidalization the diamagnetism would decrease. Also in the crystal, the resistance would increase considerably with temperature. The large increase of resistance has been observed by Roberts. [19] (Compare Robert's paper, page 174.)

(3). *The 2+3 Valencies of bismuth and antimony and their diamgnetism.*

In the case of bismuth and antimony, the contribution due to the core is larger than in carbon, due to the large number of electrons in the same, the atomic numbers being 51 and 83 for Sb and Bi respectively. The nearest rare gases with complete cores are Xe and Nt ; but so far as I am aware, we have no experimental value for the diamagnetism of these gases. The core contribution may be obtained from the ionic values but these have also been found to vary and not sufficiently accurate for a quantitative basis.[20]

Regarding the two metals in the crystalline form, here also we have a case where in the crystal of the elements, there are two different groups of unequal valencies.[21] The existence of such unequal valency orbits would explain the high magnetic anisotropy and the anomalies in analogy with graphite. The crystal structures are also similar.

[18] Honda, *loc, cit.*

[19] *loc. cit.*

[20] Further investigations are in progress for obtaining more reliable information.

[21] See also Bragg, X-rays and Crystal Structure, 5th edition, pp. 172, 189, 190.

Element.	α.	a : c
Graphite (Rhombohedral trigonal.)	85° 6′	1 : 2·3
Bismuth ,, ,,	87° 34′	1 : 1·3
Antimony ,, ,,	86° 58′	1 : 1·32

It is also important to note that in graphite, bismuth and antimony crystals, even the coefficient of linear expansion is considerably large and this is strikingly in the c axis direction.[21]

The various effects observed in anomalous diamagnetics are thus in perfect agreement with their similarity in other properties.

4. *Summary and Conclusion.*

1. Colloids of graphite, bismuth and antimony have been magnetically investigated. These elements possessing respectively an anomalous diamagnetism of $61{\cdot}2\times10^{-6}$ (mean value of the purified graphite powder at atmospheric temperature) 250×10^{-6} and 93×10^{-6} for " regulus " at atmospheric temperature, showed a decrease of diamagnetism on colloidalization. This decrease was most striking in graphite and less in bismuth and antimony. In order to avoid chemical action these have been mechanically colloidalised and the centrifuged powder was dried and investigated.

2. The anisotropy of many single natural crystals of graphite was investigated. These varied slightly, but the best crystal gave an anisotropy of $1 : 6{\cdot}7$ when the c axis was $\perp$ and $\parallel$ to the field respectively.

3. In the compounds of bismuth and antimony, the ionic values are pointed out to be much smaller than in the crystal state—26×10^{-6} for Sb^{iii}; -66×10^{-6} for Sb^{v}

[21] See also Bragg, X-rays and Crystal Structure, 5th edition, pp. 172, 189, 190.

-40×10^{-6} for Bi^{III}, and -69×10^{-6} for Bi^{V} and -6×10^{-6} for carbon in compounds. The ionic values deduced from different compounds of bismuth and antimony were found to vary.

4. The decrease in colloidalization is interpreted as due to the existence of large electron orbits comprising groups of molecules in the macrocrystal, the valency electron circuits in these equipotential surfaces being also the conducting surfaces. Such a circuit in the crystal of graphite comprises a minimum of 19 benzene rings in the cleavage plane. From the magnetic standpoint, amorphous carbon may be considered as micro-crystalline graphite and this is in conformity with the ideas of Debye and Scherrer, from their X-ray investigations of graphite and amorphous carbon.

5. The magnetic anisotropy of these elements is pointed out as due to the unequal valency groups (3+1) and (3+2) for graphite and for bismuth and antimony respectively. The anomalous diamagnetism of these elements is in perfect harmony with the similarity of crystal structure and other properties.

In conclusion, I have great pleasure in expressing my heartfelt thanks to Sir C. V. Raman for his keen interest in the problem and for providing the electro-magnet to carry on the investigations at the Annamalai University. I am no less indebted to the Vice-Chancellor, Mr. Ranganadhan for his kindness and encouragement.